

# Local thermodynamics and the generalized Gibbs-Duhem equation in systems with long-range interactions

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**Abstract.** The local thermodynamics of a system with long-range interactions in  $d$  dimensions is studied using the mean field approximation. Long-range interactions are introduced through pair interaction potentials that decay like a power law in the interparticle distance. We compute the local entropy, Helmholtz free energy and grand potential per particle in the microcanonical, canonical and grand canonical ensembles, respectively. The one-particle distribution function approach is also considered. From the local entropy per particle we obtain the local equation of state of the system by using the condition of local thermodynamic equilibrium. This equation of state turns out to be the ideal gas equation of state regardless of the pair interaction potential characterizing the long-range interactions. By volume integration of the relation between the different thermodynamic potentials at the local level, we find the corresponding equation satisfied by the potentials at the global level. It is shown that the potential energy enters as a thermodynamic variable which modifies the global thermodynamic potentials. As a result, we find a generalized Gibbs-Duhem equation which relates the potential energy to the intensive variables of the system. For the marginal case where the power of the decaying interaction potential is equal to the dimension of the space, the usual Gibbs-Duhem equation is recovered. As examples of application of this equation, we consider spatially uniform interaction potentials and the self-gravitating gas. We also point out a close relationship with the thermodynamics of small systems.

PACS numbers: 05.70.Ce, 05.20.-y, 64.10.+h, 04.40.-b

## 1. Introduction

A great variety of systems in nature are dominated by long-range interactions. Examples are self-gravitating systems [1–4], two-dimensional vortices [5], nuclear physics [6] and also toy models such as the Hamiltonian mean field model [7]. Among other physical properties, the remarkable thermodynamic behaviour of systems with long-range interactions makes them extremely attractive. They are intrinsically non-additive and may have negative heat capacity in the microcanonical ensemble leading to ensemble inequivalence [8–10]. For very instructive reviews on the subject with more examples and phenomena we refer to [10, 11].

Interactions in this kind of systems are characterized by slowly-decaying pair interaction potentials that couple the constituent parts of the system at large distances. Formally, a potential that decays as  $1/r^\nu$  is said to be long-range if  $\nu \leq d$ , where  $d$  is the dimension of the embedding space [10]. Systems having such interaction potentials are sometimes called systems with strong long-range interactions [11]. The paradigmatic case of Newtonian gravity ( $\nu = 1$ ) has served as a basis for developing methods for studying an important part of the phenomenology concerning the thermodynamics of systems with long-range interactions. In this regard, the isothermal spheres model has been widely used to study self-gravitating systems in the mean field limit [4, 12]. Although in the mean field approach correlations are ignored, this model offers a mathematical tool for a suitable treatment of self-interactions in the system and turns out to be very accurate in the thermodynamic limit [13, 14], except near the critical points where the system collapses. It is also well known that self-gravitating systems possess equilibrium states with negative heat capacity, provided the system is isolated (microcanonical ensemble). Equilibrium in that case is ensured in a certain range in the space of parameters because isothermal spheres correspond to local maxima of the entropy with an extremely large lifetime that scales like the exponential of the number of particles: strictly speaking, they are metastable states [15]. In the microcanonical ensemble the system becomes unstable when the heat capacity passes from negative to positive, leading to the gravothermal catastrophe [2, 16]. When one of these systems is put in contact with a heat bath (canonical ensemble), the range in the space of parameters where the heat capacity is negative is replaced by a phase transition [3]. In the canonical ensemble, mean field isothermal spheres correspond to states of local minima of the free energy and the isothermal collapse sets in when the heat capacity passes from positive to negative [12]. The self-gravitating gas has also been studied in the grand canonical ensemble with the mean field approach and Monte Carlo simulations. There, the instability sets in at a critical value of the parameter controlling the state of the system which is different from the critical values in the microcanonical and canonical ensembles [13, 14]. This illustrates the fact that different ensemble representations are, in general, inequivalent and the thermodynamic behaviour of the system strongly depends on the control parameter used to specify its thermodynamic state. In addition, systems with an attractive interaction potential  $1/r^\nu$  with  $0 < \nu < 3$  in 3 dimensions were also considered in the microcanonical ensemble [17, 18] and also there a critical energy was found below which these systems undergo a gravitational-like phase transition.

Moreover, de Vega and Sánchez obtained [14] the equation of state of the self-gravitating gas and pointed out that it was customary to assume it without any derivation. To obtain the equation of state they took into account the condition of hydrostatic equilibrium and found that the system locally behaves as an ideal gas. The

same result is also found using the condition of hydrostatic equilibrium for a system with arbitrary long-range interactions in the mean field limit [19].

In this framework, our aim here is, on one hand, to analyze the local thermodynamics of systems with strong long-range interactions in  $d$  dimensions by computing the local thermodynamic potentials per particle in the mean field limit. By volume integration of the relation between the different thermodynamic potentials at the local level, we find the corresponding equation satisfied by the potentials at the global level. The local equation of state is obtained by computing the local entropy per particle and using the condition of local thermodynamic equilibrium instead of assuming hydrostatic equilibrium. Although in this case the two equilibrium conditions lead to the same result, both approaches are conceptually different. On the other hand, it is shown that the potential energy enters as a thermodynamic variable which modifies the global thermodynamic potentials. As a result, we find a generalized Gibbs-Duhem equation which relates the potential energy to the intensive variables of the system. For the marginal case where the power of the decaying interaction potential is equal to the dimension of the space, the usual Gibbs-Duhem equation is recovered.

The rest of the paper is organized as follows. In section 2, we consider a system with strong long-range interactions in  $d$  dimensions and compute the local entropy, Helmholtz free energy and grand potential per particle in the microcanonical, canonical and grand canonical ensembles, respectively. We also consider the one-particle distribution function approach. In section 3, we obtain local relations satisfied by the thermodynamic potentials as well as the local equation of state. In section 4, the global equation of state is obtained for a  $d$ -dimensional system and by integrating the local relations, an equation satisfied by the set of global thermodynamic potentials is found. We also obtain the generalized Gibbs-Duhem equation and consider some examples of its application. In connection with the latter, we point out a close relationship existing between our treatment and Hill's [20] thermodynamics of small systems. Finally, in section 5, a discussion of our results is presented. We will use units such that  $k_B = 1$ .

## 2. Mean field local thermodynamic potentials

In this section we will compute the mean field local entropy, Helmholtz free energy and grand potential per particle in the microcanonical, canonical and grand canonical ensembles, respectively. Since the long-range character of the interactions depends on the dimension of the embedding space, we will consider the system is  $d$ -dimensional. Interactions are introduced through a long-range pair interaction potential  $\phi(\mathbf{q}_i, \mathbf{q}_j)$  which depends on  $\mathbf{q}_i$  and  $\mathbf{q}_j$ , the positions of particles  $i$  and  $j$ . Although here it is not necessary to make explicit the form of the interaction potential, we will formally assume that at large enough distances it behaves as

$$\phi(\mathbf{q}_i, \mathbf{q}_j) = \kappa |\mathbf{q}_i - \mathbf{q}_j|^{-\nu}, \quad (1)$$

where  $\kappa$  is a coupling constant and  $0 \leq \nu \leq d$ . This power law for the interaction, however, will be considered in Section 4 to derive global thermodynamic properties of the system. At the end of this section, we will briefly discuss how to compute local magnitudes with the one-particle distribution function approach, obtaining also the local entropy per particle.

### 2.1. Local entropy: microcanonical ensemble

Consider a system of  $N$  classical point-like particles of equal mass  $m$  enclosed in a container of  $d$ -dimensional volume  $V \sim L^d$ ,  $L$  being a characteristic length defining the size of the system. Positions and momenta of particles are respectively described by  $\mathbf{q}_i = (q_i^1, q_i^2, \dots, q_i^d)$  and  $\mathbf{p}_i = (p_i^1, p_i^2, \dots, p_i^d)$ ,  $1 \leq i \leq N$ . The Hamiltonian of the system is

$$H_N(\mathbf{q}_i, \mathbf{p}_i) = E_0 + W, \quad (2)$$

where the kinetic and potential energies,  $E_0$  and  $W$ , respectively, are given by

$$E_0 = \sum_i^N \frac{|\mathbf{p}_i|^2}{2m} \quad \text{and} \quad W = \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j). \quad (3)$$

In the microcanonical description the state of the system is characterized by a fixed value of the energy  $E$  and the number of accessible microstates with energy  $E > H_N$  in  $d$  spatial dimensions is given by

$$\Sigma(E) = \frac{1}{(2\pi\hbar)^{dN} N!} \int d^{2dN} \tau \, \theta \left( E - \sum_i^N \frac{|\mathbf{p}_i|^2}{2m} - \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j) \right), \quad (4)$$

where  $d^{2dN} \tau \equiv \prod_{i=1}^N d^d \mathbf{p}_i d^d \mathbf{q}_i$  and  $\theta(x)$  is the Heaviside step function. The domain of spatial integrations extend over the  $d$ -dimensional volume  $V$  and there are no restrictions on the domain of the momenta; this will always be the case throughout the paper unless another domain is specified. Accordingly, the microcanonical entropy is given by  $S(E) = \ln \Sigma(E)$ . Introducing

$$\mathcal{E} = \varepsilon^{-1} E, \quad \varepsilon \equiv \frac{2\pi\hbar^2}{mV^{2/d}}, \quad (5)$$

and integrating over momenta we have

$$\begin{aligned} \Sigma(E) &= \frac{1}{N! \Gamma(dN/2 + 1)} \int \frac{d^{dN} \mathbf{q}}{V^N} \\ &\times \left( \mathcal{E} - \varepsilon^{-1} \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j) \right)^{dN/2} \theta \left( \mathcal{E} - \varepsilon^{-1} \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j) \right), \end{aligned} \quad (6)$$

where  $d^{dN} \mathbf{q} \equiv \prod_{i=1}^N d^d \mathbf{q}_i$  and  $\Gamma(x)$  is the Gamma function. Using the integral representation [13]

$$x^\gamma \theta(x) = \frac{\Gamma(\gamma + 1)}{2\pi} \int_{-\infty}^{\infty} dk \frac{\exp(ikx)}{(ik)^{\gamma+1}}, \quad (7)$$

(6) becomes

$$\begin{aligned} \Sigma(E) &= \frac{1}{2\pi N!} \int \frac{d^{dN} \mathbf{q}}{V^N} \int_{-\infty}^{\infty} dk \\ &\times \exp \left[ ik \left( \mathcal{E} - \varepsilon^{-1} \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j) \right) - \left( \frac{dN}{2} + 1 \right) \ln(ik) \right]. \end{aligned} \quad (8)$$

For convenience, let us introduce the parameter  $\beta$  according to  $\varepsilon\beta = ik$  and define

$$e^{J(\beta)} \equiv \frac{1}{N!} \int \frac{d^d N \mathbf{q}}{V^N} \exp \left( -\beta \sum_{i>j}^N \phi(\mathbf{q}_i, \mathbf{q}_j) - \frac{dN}{2} \ln(\varepsilon\beta) \right), \quad (9)$$

so that (8) can be rewritten as

$$\Sigma(E) = \varepsilon \int_{-i\infty}^{i\infty} \frac{d\beta}{2\pi i} \exp [\beta E + J(\beta) - \ln(\varepsilon\beta)]. \quad (10)$$

To evaluate (9), we will employ a general method which was previously used in the context of long-range interacting systems to treat Newtonian gravity in  $d = 3$  [3, 13]. The method assumes that for long-range potentials the interactions of particles with near neighbours are negligible as compared with the interactions with the rest of more distant particles. To implement this method, the  $d$ -dimensional volume  $V$  is divided in  $M$  cells,  $1 \ll M \ll N$ , of volume  $v_a = V/M$ , so that  $\sum_{a=1}^M v_a = V$ . Each cell is located at  $\mathbf{x}_a = (x_a^1, x_a^2, \dots, x_a^d)$  and contains  $n_a \gg 1$  particles such that  $\sum_{a=1}^M n_a = N$ . This construction is self-consistent if the number of particles is large enough, i.e., it is implicitly assumed that  $N \rightarrow \infty$ . It is also assumed that the size of each cell is small enough so that the potential can be considered constant through the cell, but, of course, it varies from cell to cell. It follows that the total potential energy can be approximated as  $W \approx \sum_{a>b}^M n_a n_b \phi(\mathbf{x}_a, \mathbf{x}_b)$ .

Furthermore, with the help of the multinomial theorem it is not difficult to derive the following identity:

$$\frac{1}{N!} \int \frac{d^d N \mathbf{q}}{V^N} = \sum_{\{n_1, \dots, n_M\}} \delta_{N, \sum_{i=1}^M n_i} \prod_{i=1}^M \frac{1}{n_i!} \left( \frac{v_i}{V} \right)^{n_i}, \quad (11)$$

where  $\{n_1, \dots, n_M\}$  means all possible values  $n_1, n_2, \dots, n_M$  of the occupation numbers and the Kronecker delta restricts the total number of particles to  $N$ . Equation (11) can be seen as a way to perform an integral in the  $dN$ -dimensional configuration space by summing over all possible occupation number distributions through the cells of a single-particle configuration space. Thus, using the multinomial expansion one approximates (9) by

$$e^{J(\beta)} \approx \sum_{\{n_1, \dots, n_M\}} \delta_{N, \sum_{i=1}^M n_i} \prod_{i=1}^M \frac{1}{n_i!} \left( \frac{v_i}{V} \right)^{n_i} \times \exp \left( -\beta \sum_{a>b}^M n_a n_b \phi(\mathbf{x}_a, \mathbf{x}_b) - \frac{d}{2} \ln(\varepsilon\beta) \sum_{a=1}^M n_a \right). \quad (12)$$

The above approximation formulated in a discrete way allows one to obtain a continuous field representation. This continuum limit is obtained by introducing the number density, whose value in each cell is given by  $n(\mathbf{x}) = n_a/v_a$ . Consequently, summations over the cells become spatial integrals and the summation over occupation number distributions becomes a functional integration in the number density:

$$\sum_{a=1}^M \rightarrow \int \frac{d^d \mathbf{x}}{v_a} \quad \text{and} \quad \sum_{\{n_1, \dots, n_M\}} \rightarrow \int \mathcal{D}n(\mathbf{x}). \quad (13)$$

Using these prescriptions the total potential energy in the mean field limit takes the form

$$W[n] = \frac{1}{2} \int n(\mathbf{x}) n(\mathbf{x}') \phi(\mathbf{x}, \mathbf{x}') d^d \mathbf{x} d^d \mathbf{x}' . \quad (14)$$

In addition, with Stirling's approximation we also have

$$\prod_{i=1}^M \frac{1}{n_i!} \left( \frac{v_i}{V} \right)^{n_i} = \exp \left( - \int n(\mathbf{x}) \ln \frac{n(\mathbf{x}) V}{e} d^d \mathbf{x} \right) . \quad (15)$$

Therefore, taking into account that the Kronecker delta restricting the number of particles becomes a Dirac delta in the continuum limit and using the integral representation  $\delta(x) = (2\pi i)^{-1} \int_{-i\infty}^{i\infty} d\alpha e^{-\alpha x}$ , one gets

$$e^{J(\beta)} = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \int \mathcal{D}n \exp \left( \hat{J}[n; \alpha, \beta] \right) , \quad (16)$$

where we have introduced the functional  $\hat{J}[n; \alpha, \beta]$  defined by

$$\begin{aligned} \hat{J}[n; \alpha, \beta] \equiv & \alpha \left( N - \int n(\mathbf{x}) d^d \mathbf{x} \right) - \int n(\mathbf{x}) \ln \frac{n(\mathbf{x}) V}{e} d^d \mathbf{x} \\ & - \frac{1}{2} \beta \int n(\mathbf{x}) n(\mathbf{x}') \phi(\mathbf{x}, \mathbf{x}') d^d \mathbf{x} d^d \mathbf{x}' - \frac{d}{2} \ln(\varepsilon \beta) \int n(\mathbf{x}) d^d \mathbf{x} . \end{aligned} \quad (17)$$

Hence, by replacing (16) in (10), we have

$$e^{S(E)} = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \int_{-i\infty}^{i\infty} \frac{d\eta}{2\pi i} \int \mathcal{D}n \exp \left( \hat{S}[n; \alpha, \eta] \right) , \quad (18)$$

where we now have introduced the dimensionless variable  $\eta \equiv \varepsilon \beta$  and

$$\hat{S}[n; \alpha, \eta] \equiv \eta \varepsilon^{-1} E + \hat{J}[n; \alpha, \eta \varepsilon^{-1}] = \beta E + \hat{J}[n; \alpha, \beta] . \quad (19)$$

In the definition of  $\hat{S}$  we have neglected the term  $\ln(\varepsilon \beta) = \ln(\eta)$  coming from the exponential in (10), since it does not contribute in the limit  $N \rightarrow \infty$ . This is the same as assuming that the microcanonical entropy is given by the logarithm of the number of microstates or, equivalently, by the logarithm of the density of states. To proceed further, (18) will be evaluated using the saddle point approximation. That is, the value of the integral will be given by the exponential of  $\hat{S}[n_s; \alpha_s, \eta_s]$ , where  $n_s(\mathbf{x})$ ,  $\alpha_s$  and  $\eta_s$  are the number density and the value of the parameters that maximize  $\hat{S}[n; \alpha, \eta]$ . Accordingly, the microcanonical entropy can be approximated by  $S(E) \approx \hat{S}[n_s; \alpha_s, \eta_s]$ . In order to simplify the notation, in what follows we will omit the subscript s, since we will only consider the stationary solutions given by the saddle point approximation.

The parameters  $\alpha$  and  $\eta$  in (18) can be viewed as Lagrange multipliers that respectively restrict the value of the number of particles and the energy. Indeed, the mean field equations in the saddle point approximation given by the extremal condition  $(\delta_n; \partial_\alpha, \partial_\eta) \hat{S}[n; \alpha, \eta] = (0; 0, 0)$  yield

$$N = \int n(\mathbf{x}) d^d \mathbf{x} , \quad (20)$$

$$E = \frac{d}{2\beta} \int n(\mathbf{x}) d^d \mathbf{x} + W[n] \quad (21)$$

after computing the derivatives of  $\hat{S}[n; \alpha, \eta]$  with respect to  $\alpha$  and  $\eta$ . Moreover, taking into account (17), variations of the number density in (19) lead to  $\delta \hat{S}[n] = \delta \hat{J}[n]$  with

$$\delta \hat{J}[n] = \int \left[ -\beta \Phi(\mathbf{x}) - \alpha - \ln \left( n(\mathbf{x}) V \eta^{d/2} \right) \right] \delta n(\mathbf{x}) d^d \mathbf{x} , \quad (22)$$

where the term containing the potential  $\Phi(\mathbf{x})$  comes from the variation  $\delta W[n] = \int \Phi(\mathbf{x}) \delta n(\mathbf{x}) d^d \mathbf{x}$  and is given by

$$\Phi(\mathbf{x}) = \int n(\mathbf{x}') \phi(\mathbf{x}, \mathbf{x}') d^d \mathbf{x}'. \quad (23)$$

In terms of  $\Phi(\mathbf{x})$ , the total potential energy takes the form

$$W[n] = \frac{1}{2} \int n(\mathbf{x}) \Phi(\mathbf{x}) d^d \mathbf{x}. \quad (24)$$

Hence, by setting the functional derivative with respect to  $n(\mathbf{x})$  to zero,  $\delta_n \hat{S}[n] = \delta_n \hat{J}[n] = 0$ , it follows the coupling between the number density and the interaction potential through the relation

$$n(\mathbf{x}) = \lambda_T^{-d} \exp[-\beta(\Phi(\mathbf{x}) - \mu)], \quad (25)$$

where we have introduced  $\lambda_T = V^{1/d} \eta^{1/2}$  and  $\mu = -\alpha/\beta$ . As a result, by replacing (20) and (21) in (17) and (19), the extrema of  $\hat{S}$  and consequently the microcanonical mean field entropy become

$$S = \int n(\mathbf{x}) \left[ -\ln(n(\mathbf{x}) \lambda_T^d) + \frac{2+d}{2} \right] d^d \mathbf{x}, \quad (26)$$

which is an integral over the volume and therefore the integrand can be interpreted as the density of entropy. From this density of entropy one can construct the local entropy per particle and in this way, as we shall see below, information about the local thermodynamic nature of the system can be obtained. Taking into account (26), the local entropy per particle is given by

$$s(\mathbf{x}) = -\ln(n(\mathbf{x}) \lambda_T^d) + \frac{2+d}{2}, \quad (27)$$

in such a way that the total mean field entropy can be written as

$$S = \int n(\mathbf{x}) s(\mathbf{x}) d^d \mathbf{x}. \quad (28)$$

In addition, using (17) and (19), it can be checked that  $\beta$  is the inverse temperature,  $\mu$  is the chemical potential,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} = \beta, \quad -\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{E,V} = \alpha, \quad (29)$$

and that

$$\lambda_T = \left( \frac{2\pi\hbar^2}{mT} \right)^{1/2} \quad (30)$$

is the thermal wavelength.

The microcanonical mean field entropy (26) is an extremal solution of the mean field equations. In order to guarantee thermodynamic equilibrium, we will assume that there exist a certain range of parameters where  $\hat{S}$  is a maximum and thus, our analysis here must be understood restricted to such a range. It is not difficult to see that such a range in the space of parameters does exist: if the temperature is high enough so that  $\beta\Phi(\mathbf{x}) \ll 1$ , the number density becomes  $n \approx N/V$  and the stable global ideal gas behaviour is recovered. The critical values of the parameters that set the instability will depend on the interactions under consideration.

## 2.2. Local Helmholtz free energy: canonical ensemble

Here we will consider that the control parameter used to specify the equilibrium configurations is the inverse temperature  $\beta$ . At fixed temperature one must use the canonical description and in this section we will compute the canonical partition function,  $Z(\beta)$ , in the saddle point approximation. In doing so, the canonical Helmholtz free energy,  $A(\beta)$ , can be obtained and written as an integral over the volume which allows us to identify the local free energy.

The canonical partition function can be obtained from the microcanonical density of states,  $\omega_E = \partial_E \Sigma(E)$ , by computing its Laplace transform. The density of states is then given by the inverse Laplace transform of the partition function,

$$\omega_E = \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \frac{\mathrm{d}\beta}{2\pi\mathrm{i}} Z(\beta) e^{\beta E}. \quad (31)$$

By computing the derivative of expression (10) with respect to  $E$  one gets

$$\frac{\partial}{\partial E} \Sigma(E) = \int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} \frac{\mathrm{d}\beta}{2\pi\mathrm{i}} e^{J(\beta)} e^{\beta E}. \quad (32)$$

Therefore, the comparison of both expressions (31) and (32) leads to the identification

$$Z(\beta) = e^{J(\beta)}, \quad (33)$$

and thus, one sees that the function  $J(\beta)$  defined in (9) is just the Massieu function related to the Helmholtz free energy via  $J(\beta) = -\beta A(\beta)$ . Hence, the major part of the work has already been done writing down the microcanonical description, since the canonical partition function is given by (16). It is clear that the extremal condition  $(\delta_n; \partial_\alpha) \hat{J}[n; \alpha, \beta] = (0; 0)$  allows one to get an approximate expression for the Massieu function as  $J(\beta) \approx \hat{J}[n; \alpha, \beta]$ , where, as before,  $n(\mathbf{x})$  and  $\alpha$  are given by the saddle point equations. The saddle point equation associated with the parameter  $\alpha$  constrains the number of particles leading to the condition (20). Of course, in the canonical description only the temperature is fixed and there is no second Lagrange multiplier enforcing the condition (21). Instead, according to the saddle point approximation and using (17), one sees that the mean value of the Hamiltonian  $\langle E \rangle = -\partial_\beta \ln Z \approx -\partial_\beta \hat{J} \equiv \bar{E}$ , becomes

$$\bar{E} = \frac{d}{2\beta} \int n(\mathbf{x}) \mathrm{d}^d \mathbf{x} + W[n] \quad (34)$$

in the mean field limit.

On the other hand, in order to obtain the relation between the number density and the interaction potential, variations with respect to the number density of  $\hat{J}[n]$  has to be computed. This task has also been done in the previous section and  $\delta \hat{J}[n]$  is given by expression (22). As a result, the distribution of particles that maximizes the microcanonical entropy also maximizes the Massieu function in the canonical ensemble and the number density is then given by (25). Hence, using (17), (20) and (24), the saddle point approximation allows one to write the canonical mean field Helmholtz free energy  $A = -TJ$  as an integral over the volume in the mean field limit:

$$A = \int n(\mathbf{x}) \left\{ T [\ln (n(\mathbf{x}) \lambda_T^d) - 1] + \frac{1}{2} \Phi(\mathbf{x}) \right\} \mathrm{d}^d \mathbf{x}. \quad (35)$$

Therefore, the mean field local Helmholtz free energy is readily identified,

$$a(\mathbf{x}) = T [\ln (n(\mathbf{x}) \lambda_T^d) - 1] + \frac{1}{2} \Phi(\mathbf{x}), \quad (36)$$



since

$$A = \int n(\mathbf{x})a(\mathbf{x})d^d\mathbf{x}. \quad (37)$$

The canonical mean field entropy can be obtained via a Legendre transformation of the canonical mean field free energy,  $S = \beta(\bar{E}A)$ , and, as a consequence of the saddle point approximation [6], it coincides with the microcanonical mean field entropy (26). The mean field solution in the canonical ensemble is valid only in the range of parameters where  $\hat{J}$  is maximum.

### 2.3. Local grand potential: grand canonical ensemble

Consider the canonical partition function as a function of the number of particles and its Laplace transform:

$$\mathcal{L}[Z](\alpha) = \int_0^\infty dN Z(N) e^{-\alpha N}. \quad (38)$$

Taking  $N$  as a continuous variable, the canonical partition function is constant with value  $Z(N)$  for all  $N$  in the interval  $[N, N+1)$ . Therefore, the integral in (38) can be written as a sum of integrals over the intervals  $[N, N+1)$  and subsequently integrated:

$$\mathcal{L}[Z](\alpha) = \sum_{N=0}^\infty Z(N) \int_N^{N+1} d\tilde{N} e^{-\alpha \tilde{N}} \quad (39)$$

$$= \frac{1 - e^{-\alpha}}{\alpha} \sum_{N=0}^\infty e^{-\alpha N} Z(N). \quad (40)$$

From here, since  $\alpha = -\beta\mu$ , one recognizes the grand canonical partition function

$$\mathcal{Z}(\alpha) = \sum_{N=0}^\infty e^{-\alpha N} Z(N), \quad (41)$$

which we will take as the starting point to derive the thermodynamics of the system. Introducing  $\zeta(\alpha) = [1 - \exp(-\alpha)]/\alpha$  and applying the inverse Laplace transform to (40) one gets

$$Z(N) = \mathcal{L}^{-1}[\zeta \mathcal{Z}](N) = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \zeta(\alpha) \mathcal{Z}(\alpha) e^{\alpha N}. \quad (42)$$

Since in the previous section we obtained

$$Z(N) = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \int \mathcal{D}n \exp\left(\hat{J}[n; \alpha, \beta]\right), \quad (43)$$

the grand canonical partition function reads

$$\mathcal{Z} = \int \mathcal{D}n \exp\left(\hat{J}[n; \alpha, \beta] - \alpha N - \ln \zeta(\alpha)\right). \quad (44)$$

The term  $\ln \zeta(\alpha)$  in the exponential above, which is a correction due to the discreteness of  $N$ , can be safely neglected in the limit  $N \rightarrow \infty$ . As before, we shall evaluate the integral (44) using the saddle point approximation, hence  $\mathcal{Z} \approx \exp(\hat{J} - \alpha N)$ . In this case, only the number density such that  $\delta_n(\hat{J}[n] - \alpha N) = \delta_n \hat{J}[n] = 0$  is required. Thus, one more time the number density is given by (25). Furthermore, the mean value of

the number of particles can be written as  $\langle N \rangle = -\partial_\alpha \ln \mathcal{Z} \approx -\partial_\alpha (\hat{J} - \alpha N) \equiv \bar{N}$  and using (17) one gets

$$\bar{N} = \int n(\mathbf{x}) d^d \mathbf{x}. \quad (45)$$

Analogously, the mean value of the energy takes the form  $\langle E \rangle = -\partial_\beta \ln \mathcal{Z} \approx -\partial_\beta (\hat{J} - \alpha N) = \bar{E}$ , where, as in the canonical case,  $\bar{E}$  is given by (34). Introducing the grand potential

$$\Omega = -T \ln \mathcal{Z}, \quad (46)$$

the saddle point approximation yields  $-\beta \Omega \approx \hat{J} - \alpha N$ , which by using (17) and (24) leads to

$$\Omega = \int n(\mathbf{x}) \left\{ T [\ln (n(\mathbf{x}) \lambda_T^d) - 1] - \mu + \frac{1}{2} \Phi(\mathbf{x}) \right\} d^d \mathbf{x} \quad (47)$$

in the mean field limit. Consequently, the mean field local grand potential per particle reads

$$\omega(\mathbf{x}) = T [\ln (n(\mathbf{x}) \lambda_T^d) - 1] - \mu + \frac{1}{2} \Phi(\mathbf{x}), \quad (48)$$

such that

$$\Omega = \int n(\mathbf{x}) \omega(\mathbf{x}) d^d \mathbf{x}. \quad (49)$$

The grand canonical mean field Helmholtz free energy is obtained by a Legendre transformation of the form  $A = \Omega + \mu \bar{N}$ , which turns out to be equal to the mean field Helmholtz free energy in the canonical ensemble (35). With a subsequent Legendre transformation, we would obtain the same mean field entropy as in the microcanonical ensemble  $S = \beta(\bar{E} - \mu \bar{N} - \Omega)$ . As mentioned before, this is a consequence of the saddle point approximation. Although each ensemble has its own range of validity in the corresponding space of parameters, the thermodynamic potentials computed in the different ensembles have all the same form in the mean field limit. In the grand canonical ensemble the mean field solution is valid only in the range of parameters such that  $\hat{J} - \alpha N$  is maximum.

#### 2.4. One-particle distribution function approach

Let us consider a system of  $N$  classical particles of mass  $m$  confined in a container of volume  $V$ . These particles interact via a pair potential  $\phi(\mathbf{x}, \mathbf{x}')$  which describes the interaction between particles at positions  $\mathbf{x}$  and  $\mathbf{x}'$ . The distribution of particles is given by the stationary distribution function  $f = f(\mathbf{x}, \mathbf{p})$  defined in the  $2d$ -dimensional single-particle phase space,  $\mathbf{p}$  being the momentum. The spatial distribution of particles is given by

$$n(\mathbf{x}) = \int f(\mathbf{x}, \mathbf{p}) d^d \mathbf{p} \quad (50)$$

and the distribution function is normalized such that

$$N = \int f(\mathbf{x}, \mathbf{p}) d^d \mathbf{x} d^d \mathbf{p} = \int n(\mathbf{x}) d^d \mathbf{x}. \quad (51)$$

The energy of the system can be written in terms of the distribution function according to

$$E = E_0 + W = \int \left( \frac{|\mathbf{p}|^2}{2m} + \frac{1}{2} \Phi(\mathbf{x}) \right) f(\mathbf{x}, \mathbf{p}) d^d \mathbf{x} d^d \mathbf{p}, \quad (52)$$

where the potential  $\Phi(\mathbf{x})$  reads

$$\Phi(\mathbf{x}) = \int \phi(\mathbf{x}, \mathbf{x}') f(\mathbf{x}', \mathbf{p}') d^d \mathbf{x}' d^d \mathbf{p}' \quad (53)$$

and therefore, the total potential energy takes the form

$$W = \frac{1}{2} \int \Phi(\mathbf{x}) f(\mathbf{x}, \mathbf{p}) d^d \mathbf{x} d^d \mathbf{p} \quad (54)$$

$$= \frac{1}{2} \int \phi(\mathbf{x}, \mathbf{x}') f(\mathbf{x}, \mathbf{p}) f(\mathbf{x}', \mathbf{p}') d^d \mathbf{x} d^d \mathbf{p} d^d \mathbf{x}' d^d \mathbf{p}'. \quad (55)$$

In view of (50), it is clear that the potential and the total potential energy are given by equations (23) and (24), respectively.

Assuming that the thermodynamics of the system is obtained from the Boltzmann entropy defined by

$$S = - \int f(\mathbf{x}, \mathbf{p}) \ln \frac{f(\mathbf{x}, \mathbf{p})}{f_c} d^d \mathbf{x} d^d \mathbf{p}, \quad (56)$$

the stable configurations are those having a distribution function that maximizes this entropy. Here  $f_c$  is a constant which does not depend on the thermodynamic state of the system. The distribution function which makes the entropy be extremal is obtained by solving the variational problem

$$\delta S[f] - \alpha \delta N[f] - \beta \delta E[f] = 0, \quad (57)$$

where  $\alpha$  and  $\beta$  are Lagrange multipliers enforcing the constraints (51) and (52), respectively. The Lagrange multipliers, as before, can be identified with the chemical potential,  $\mu = -\alpha/\beta$ , and the inverse temperature,  $\beta = T^{-1}$ . One finds that the solution to the variational problem is the Maxwell-Boltzmann distribution given by  $f = f_c \exp \{-[1 + \alpha + \beta\Phi + \beta|\mathbf{p}|^2/(2m)]\}$ , which can be rewritten as

$$f(\mathbf{x}, \mathbf{p}) = \lambda_T^{-d} \left( \frac{\beta}{2\pi m} \right)^{d/2} \exp \left[ -\beta \frac{|\mathbf{p}|^2}{2m} - \beta (\Phi(\mathbf{x}) - \mu) \right], \quad (58)$$

where  $\lambda_T = (e/f_c)^{1/d} / \sqrt{2\pi m T}$ . Integration of the distribution function (58) over momenta gives the local distribution of particles in the spatial domain,

$$n(\mathbf{x}) = \int f(\mathbf{x}, \mathbf{p}) d^d \mathbf{p} = \lambda_T^{-d} \exp [-\beta (\Phi(\mathbf{x}) - \mu)], \quad (59)$$

which coincides with (25) if one set the constant  $f_c$  in  $\lambda_T$  to be  $f_c = e/(2\pi\hbar)^d$ . One also sees that

$$f(\mathbf{x}, \mathbf{p}) = n(\mathbf{x}) \left( \frac{\beta}{2\pi m} \right)^{d/2} \exp \left[ -\beta \frac{|\mathbf{p}|^2}{2m} \right]. \quad (60)$$

As in the case of the density above, any local magnitude can be obtained by integration in phase space of the corresponding microscopic contribution weighted down by the distribution function. That is, any local magnitude per particle  $q(\mathbf{x})$  associated with the global quantity  $Q$  can be defined through

$$n(\mathbf{x})q(\mathbf{x}) \equiv \int f(\mathbf{x}, \mathbf{p}) Q(\mathbf{x}, \mathbf{p}) d^d \mathbf{p} \quad (61)$$

provided

$$Q = \int f(\mathbf{x}, \mathbf{p}) Q(\mathbf{x}, \mathbf{p}) d^d \mathbf{x} d^d \mathbf{p}. \quad (62)$$

In the case of the entropy, e.g., one takes  $\mathcal{S}(\mathbf{x}, \mathbf{p}) = -\ln(f(\mathbf{x}, \mathbf{p})/f_c)$  which after integration using (60) gives

$$\int f(\mathbf{x}, \mathbf{p}) \mathcal{S}(\mathbf{x}, \mathbf{p}) d^d \mathbf{p} = n(\mathbf{x}) \left[ -\ln(n(\mathbf{x}) \lambda_T^d) + \frac{2+d}{2} \right]. \quad (63)$$

The term in brackets coincides with (27), the mean field local entropy obtained in the ensemble representations. By Legendre transforming the mean field entropy, all the other mean field thermodynamic potentials can be obtained. Thus, the ensemble representations and the one-particle distribution function approach give the same mean field local thermodynamic potentials.

Depending on the boundary conditions given by the control parameter, the thermodynamic equilibrium is ensured if the corresponding thermodynamic potential is maximum. If the system is isolated with fixed energy  $E$ , then the conditions on the stability of the mean field solution are found by considering second order perturbations of the entropy  $S$ . On the other hand, if the system is in contact with a heat bath which fixes the temperature, second order perturbations of the Massieu function  $J = S - \beta \bar{E}$  must be considered, with  $\bar{E} = E$  given by (52). If, in addition, the number of particles fluctuates constrained by a given value of the chemical potential, the stability is guaranteed if the quantity  $J - \alpha \bar{N}$ , with  $\bar{N} = N$  given by (51), is a maximum. Therefore, in this case second order perturbations of  $J - \alpha \bar{N}$  have to be taken into account.

### 3. Local relations and the local equation of state

In the previous sections we wrote the thermodynamic potentials as integrals over the volume of the system, which leads to a natural definition of local quantities per particle. Analogously, using (21) and (24), the local energy per particle takes the form

$$e(\mathbf{x}) = e_0 + \frac{1}{2} \Phi(\mathbf{x}), \quad (64)$$

where  $e_0$  is the local kinetic energy per particle,

$$e_0 = \frac{d}{2} T, \quad (65)$$

such that the total energy and kinetic energy are given by

$$E = \int n(\mathbf{x}) e(\mathbf{x}) d^d \mathbf{x}, \quad (66)$$

$$E_0 = \int n(\mathbf{x}) e_0 d^d \mathbf{x}. \quad (67)$$

We also introduce the local volume per particle,  $v(\mathbf{x})$ , given by

$$v(\mathbf{x}) = \frac{1}{n(\mathbf{x})}, \quad (68)$$

since, obviously,  $V = \int n(\mathbf{x}) v(\mathbf{x}) d^d \mathbf{x}$ .

Once local variables are defined, the local equation of state can be obtained. In order to do that, it is useful to write the local entropy per particle in a more convenient way. Using (30), (65) and (68), from (27) one obtains

$$s(\mathbf{x}) = \ln \left[ v(\mathbf{x}) \left( \frac{m}{d\pi\hbar^2} e_0 \right)^{d/2} \right] + \frac{2+d}{2}, \quad (69)$$

which is the Sackur-Tetrode equation in  $d$  dimensions formulated in terms of local variables. The local entropy per particle is therefore explicitly obtained as a function of the local variables  $e_0$  and  $v$ ,  $s = s(e_0, v)$ . Thus, in the equilibrium framework, one infers that the local internal energy only has contributions coming from kinetic degrees of freedom while self-interactions play the role of an external field that perturbs the gas. In addition, local thermodynamic equilibrium implies the relations [21, 22]

$$\frac{1}{T} = \left( \frac{\partial s}{\partial e_0} \right)_v \quad \text{and} \quad \frac{p}{T} = \left( \frac{\partial s}{\partial v} \right)_{e_0}, \quad (70)$$

where the second of these relations is the local equation of state of the system. In our case, this local equation of state is indeed the one corresponding to an ideal gas,

$$p(\mathbf{x}) = n(\mathbf{x})T, \quad (71)$$

which is valid for any long-range pair interaction potential that can be suitably represented with the mean field approach. Since the mean field local entropy per particle takes the same functional form in the microcanonical, canonical and grand canonical ensembles, the above equation of state is valid in the three ensembles. Notice that the condition of local thermodynamic equilibrium together with expressions (70) are formulated as a hypothesis in the framework of non-equilibrium thermodynamics, but here they are trivially satisfied provided the whole system is in equilibrium.

To get more insight in the relation between local thermodynamic variables, we use (25) and write the chemical potential as

$$\mu = \mu_0(\mathbf{x}) + \Phi(\mathbf{x}), \quad (72)$$

where

$$\mu_0(\mathbf{x}) = T \ln(\lambda_T^d n(\mathbf{x})) \quad (73)$$

possesses the same functional dependence on the number density as the chemical potential of an ideal gas, but with the density given by (25). Also using (25), the local entropy per particle can be rewritten as

$$s(\mathbf{x}) = \frac{1}{T} \left( \frac{d}{2} T + \Phi(\mathbf{x}) \right) + 1 - \frac{\mu}{T}, \quad (74)$$

and because  $p(\mathbf{x})v(\mathbf{x}) = T$  one obtains

$$Ts(\mathbf{x}) = [e_0 + \Phi(\mathbf{x})] + p(\mathbf{x})v(\mathbf{x}) - \mu. \quad (75)$$

The term in brackets is the total energy of a particle at the point  $\mathbf{x}$ ; locally the potential  $\Phi(\mathbf{x})$  acts like an external field. However, the difference between  $\Phi(\mathbf{x})$  and an authentic external field becomes manifest when one sums the contribution of the whole system: multiplying  $[e_0 + \Phi(\mathbf{x})]$  by the density and integrating over the volume does not give the total energy. In order to obtain the total energy one must take into account that the total potential energy is due to self-interactions and this is the reason why one defines the local energy per particle according to (64) (the total potential energy is a functional quadratic in the density). In this respect, using (64), equation (75) can be alternatively written in the form

$$Ts(\mathbf{x}) = e(\mathbf{x}) + p(\mathbf{x})v(\mathbf{x}) - \mu + \frac{1}{2}\Phi(\mathbf{x}), \quad (76)$$

where the last term highlights the fact that self-interactions are actually considered. Nonetheless, the statement that particles behave locally as an ideal gas can also be seen by rewriting (75) explicitly in the form

$$Ts(\mathbf{x}) = e_0 + p(\mathbf{x})v(\mathbf{x}) - \mu_0(\mathbf{x}). \quad (77)$$

The local Helmholtz free energy per particle,  $a(\mathbf{x})$ , can be obtained by the Legendre transformation

$$a(\mathbf{x}) = e(\mathbf{x}) - Ts(\mathbf{x}) = \mu - p(\mathbf{x})v(\mathbf{x}) - \frac{1}{2}\Phi(\mathbf{x}). \quad (78)$$

It can be checked that (78) coincides with (36). The local Helmholtz free energy per particle can also be written in the form

$$a(\mathbf{x}) = a_0(\mathbf{x}) + \frac{1}{2}\Phi(\mathbf{x}), \quad (79)$$

where  $a_0(\mathbf{x})$  is the local Helmholtz free energy per particle of an ideal gas at the point  $\mathbf{x}$ , which is given by

$$a_0(\mathbf{x}) = -T [\ln(v(\mathbf{x})\lambda_T^{-d}) + 1]. \quad (80)$$

Hence, it also satisfies

$$a_0(\mathbf{x}) = e_0 - Ts(\mathbf{x}) = \mu_0(\mathbf{x}) - p(\mathbf{x})v(\mathbf{x}). \quad (81)$$

Moreover, the local grand potential (48) is equivalent to the Legendre transformation  $\omega(\mathbf{x}) = a(\mathbf{x}) - \mu$  and with elementary manipulations it can be rewritten as

$$\omega(\mathbf{x}) = -p(\mathbf{x})v(\mathbf{x}) - \frac{1}{2}\Phi(\mathbf{x}). \quad (82)$$

The local grand potential per particle of an ideal gas takes the form

$$\omega_0(\mathbf{x}) = a_0(\mathbf{x}) - \mu_0(\mathbf{x}) = -p(\mathbf{x})v(\mathbf{x}), \quad (83)$$

so that it is related with  $\omega(\mathbf{x})$  through

$$\omega(\mathbf{x}) = \omega_0(\mathbf{x}) - \frac{1}{2}\Phi(\mathbf{x}). \quad (84)$$

By replacing (82) in (49) and using the local equation of state one sees that the total grand potential is closely related to the kinetic and potential energies,

$$\Omega = - \int p(\mathbf{x}) d^d \mathbf{x} - W = -\frac{2}{d}E_0 - W. \quad (85)$$

It is worth noting that the Legendre transformation of a local variable with respect to the local volume, in general, does not agree with the corresponding Legendre transformation of the global variable with respect to the total volume. The reason is that, in general, the pressure is not uniform, in contrast with the other intensive variables  $\mu$  and  $T$ . For instance, integration of the quantity

$$\tilde{g}(\mathbf{x}) \equiv a(\mathbf{x}) + p(\mathbf{x})v(\mathbf{x}) = \mu - \frac{1}{2}\Phi(\mathbf{x}), \quad (86)$$

that is,

$$\tilde{G} = \int n(\mathbf{x})\tilde{g}(\mathbf{x}) d^d \mathbf{x} = A + \frac{2}{d}E_0 = \mu N - W, \quad (87)$$

does not coincide with the total Gibbs free energy  $G = A + PV$  when long-range interactions make the system be inhomogeneous. Here  $P = p(\mathbf{x})|_{\mathbf{x} \in \partial V}$  is the pressure evaluated at the boundary of the  $d$ -dimensional system. The quantity  $PV$  depends on the total value of the potential energy and its functional relation with the total kinetic energy; e.g., in the case of Newtonian gravity in  $d = 3$  one has  $2E_0 + W = 3PV$ . An analogous situation occurs if the enthalpy  $H = E + PV$  is considered.

In the next section, the global equation of state and an expression for the total Gibbs free energy will be obtained for systems in spherical containers with interaction potentials of the form (1). In such cases, the local Gibbs free energy can be trivially derived from the global free energy  $G$ .

#### 4. Global magnitudes and the generalized Gibbs-Duhem equation

Useful relations between global quantities can be obtained by integration of the local equations. Multiplying both sides of (76) by  $n(\mathbf{x})$  and integrating over the volume yields

$$TS = E + \frac{2}{d}E_0 - \mu N + W. \quad (88)$$

However, it would be desirable that the quantity  $PV$  appears explicitly related to the other thermodynamic quantities. In order to do that, the form of the pair interaction potential has to be considered. We shall see that once the quantity  $PV$  is explicitly introduced, not only the Gibbs free energy can be computed but also the Gibbs-Duhem equation satisfied by the system.

We will consider that the container is a  $(d-1)$ -sphere of radius  $R$ , in such a way that particles are confined by the boundary condition  $(q_i^1)^2 + (q_i^2)^2 + \dots + (q_i^d)^2 \leq R^2$ ,  $1 \leq i \leq N$ . The 0-sphere is the pair of endpoints of the line segment of length  $2R$ . Besides, the volume of the system reads  $V = \pi^{d/2} R^d [\Gamma(d/2 + 1)]^{-1}$ .

Thus, from (6), using coordinates defined according to  $\mathbf{r}_i = \mathbf{q}_i/R$  and rescaling energies by introducing [13, 18]

$$\Lambda \equiv \frac{ER^\nu}{|\kappa|N^2} = \frac{E}{|\kappa|N^2} \left( \frac{\Gamma(d/2 + 1)}{\pi^{d/2}} V \right)^{\nu/d}, \quad (89)$$

$$\varphi(\mathbf{r}_i, \mathbf{r}_j) \equiv \frac{R^\nu}{|\kappa|N^2} \phi(\mathbf{q}_i, \mathbf{q}_j) = \frac{1}{N^2} \frac{\kappa}{|\kappa|} |\mathbf{r}_i - \mathbf{r}_j|^{-\nu}, \quad (90)$$

the entropy takes the form

$$S = \ln \frac{V^{N(2-\nu)/2}}{\vartheta} + \ln \tilde{\Sigma}(\Lambda). \quad (91)$$

Here

$$\vartheta = \left( \frac{2\pi\hbar^2}{N^2|\kappa|m} \right)^{dN/2} \left( \frac{\pi^{d/2}}{\Gamma(d/2 + 1)} \right)^{N(2-\nu)/2} \quad (92)$$

and

$$\begin{aligned} \tilde{\Sigma}(\Lambda) &= \frac{1}{N! \Gamma(dN/2 + 1)} \int_D d^{dN} \mathbf{r} \\ &\times \left( \Lambda - \sum_{i>j}^N \varphi(\mathbf{r}_i, \mathbf{r}_j) \right)^{dN/2} \theta \left( \Lambda - \sum_{i>j}^N \varphi(\mathbf{r}_i, \mathbf{r}_j) \right). \end{aligned} \quad (93)$$

Notice that  $\tilde{\Sigma}(\Lambda)$  depends on the volume only through  $\Lambda$ , since in the  $\mathbf{r}_i$ -coordinates, which belong to a certain domain  $D$ , the limits of the integrals in (93) are pure numbers. Taking into account that  $(\partial_E \Lambda)_V = \Lambda/E$  and  $(\partial_V \Lambda)_E = \nu \Lambda/(dV)$ , one has

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V = \frac{\Lambda}{E} \frac{\partial \ln \tilde{\Sigma}(\Lambda)}{\partial \Lambda}, \quad (94)$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_E = \frac{N}{V} \left( 1 - \frac{\nu}{2} \right) + \frac{\nu \Lambda}{dV} \frac{\partial \ln \tilde{\Sigma}(\Lambda)}{\partial \Lambda}, \quad (95)$$

where  $P = p(\mathbf{x})|_{\mathbf{x} \in \partial V}$ . From the above equations and using that  $E = E_0 + W$  one gets

$$\frac{PV}{NT} = 1 + \nu \frac{W}{dNT}, \quad (96)$$

which is the exact microcanonical equation of state of the system. However, in the mean field limit this equation holds also in the canonical and grand canonical ensembles if mean values are taken such that  $\bar{E} = E$  and  $\bar{N} = N$ . Of course, the last statement is only valid in the domain of the space of parameters where each ensemble representation is well defined. With this in mind, for simplicity, in what follows we will not distinguish between  $E$  and  $\bar{E}$  or  $N$  and  $\bar{N}$ .

From the equation of state (96) the virial theorem is obtained,

$$2E_0 + \nu W = dPV, \quad (97)$$

which is particularly useful to express the relation between global quantities. It is also useful to introduce the long-range parameter  $\sigma$  defined as

$$\sigma \equiv \frac{d - \nu}{d}, \quad 0 \leq \sigma \leq 1, \quad (98)$$

which together with (97) enables us to rewrite (88) in the form

$$TS = E + PV - \mu N + \sigma W. \quad (99)$$

The marginal case  $\nu = d$  correspond to systems with long-range parameter  $\sigma = 0$ , so that the above equation and the thermodynamic potentials obtained below reduce to the usual ones in short-range interactions thermodynamics. The Helmholtz free energy, the grand potential and the Gibbs free energy are readily obtained from (99) and take the form

$$A = E - TS = \mu N - PV - \sigma W, \quad (100)$$

$$\Omega = A - \mu N = -PV - \sigma W, \quad (101)$$

$$G = A + PV = \mu N - \sigma W. \quad (102)$$

The above expressions generalize previous results for the self-gravitating gas [13, 14]. In addition, by differentiating (99) one gets

$$TdS = dE + PdV - \mu dN + \sigma dW - Nd\mu - SdT + VdP \quad (103)$$

and since  $TdS = dE + PdV - \mu dN$  we must have

$$\sigma dW = SdT - VdP + Nd\mu, \quad (104)$$

which is the generalized Gibbs-Duhem equation satisfied by the long-range interacting systems we are considering here. For systems with long-range parameter  $\sigma = 0$ , i.e. the marginal case  $\nu = d$ , the usual Gibbs-Duhem equation is recovered. From (104) we infer that when long-range interactions are present, the intensive variables are independent. Moreover, in view of (104), the following relations are obtained for  $\sigma \neq 0$ :

$$\sigma \left( \frac{\partial W}{\partial T} \right)_{P, \mu} = S, \quad \sigma \left( \frac{\partial W}{\partial P} \right)_{T, \mu} = -V, \quad \sigma \left( \frac{\partial W}{\partial \mu} \right)_{P, T} = N. \quad (105)$$

The above expressions imply, for instance, that the entropy can be obtained from a derivative of the potential energy. Since such thermodynamic relations have not been reported previously for systems with long-range interactions, it would be interesting to check them by considering some solvable examples. Next, we will consider the case where the interaction potential is spatially uniform and the case where the system is a self-gravitating gas. After these two examples we will expose a common feature between systems with long-range interactions and small systems.



#### 4.1. Spatially uniform interaction potentials in $d$ dimensions

These systems are characterized by  $\nu = 0$  such that the system is homogeneous and  $\sigma = 1$ . We simply have  $\phi = \kappa$ , hence  $\Phi = kN$  and  $W = \kappa N^2/2$ . In order to apply (105), the potential energy must be written as a function of the intensive variables,  $W = W(T, P, \mu)$ . Using (25) and the equation of state (96), which in this case reads  $PV = NT$ , one obtains  $n = N/V = P/T = \lambda_T^{-d} \exp[-\beta(\kappa N - \mu)]$  and the number of particles becomes

$$N = \frac{1}{\kappa} \left[ \mu - T \ln \left( \frac{P \lambda_T^d}{T} \right) \right]. \quad (106)$$

The potential energy then takes the form

$$W(T, P, \mu) = \frac{1}{2\kappa} \left[ \mu - T \ln \left( \frac{P \lambda_T^d}{T} \right) \right]^2. \quad (107)$$

Taking into account that the local entropy per particle (27) is uniform in this case, whence  $S = Ns$ , it is straightforward to see that

$$S = \left( \frac{\partial W}{\partial T} \right)_{P, \mu} = \frac{1}{\kappa} \left[ \mu - T \ln \left( \frac{P \lambda_T^d}{T} \right) \right] \left[ -\ln \left( \frac{P \lambda_T^d}{T} \right) + \frac{2+d}{2} \right].$$

The remaining two relations (105) follow from  $V = NT/P$  and (106).

#### 4.2. Self-gravitating isothermal spheres in $d = 3$

The calculation of global thermodynamic quantities of self-gravitating isothermal spheres is well understood and here we will just consider it as an example to illustrate the relations (105). In particular, the first of these relations will be used to obtain the entropy of the self-gravitating gas. We will write down only the necessary expressions to carry out our task and refer the reader to [4, 12, 15] for details.

In the self-gravitating gas we have  $\nu = 1$ , thus  $\sigma = 2/3$ , and  $\kappa = -G_N m^2$ , where  $G_N$  is Newton's constant. Also, Newtonian systems satisfy the Poisson-Boltzmann equation which, after introducing the dimensionless variables  $\xi = (4\pi|\kappa|\beta n(0))^{1/2}x$  and  $\psi = \beta(\Phi(x) - \Phi(0))$ , becomes the Emden equation

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left( \xi^2 \frac{d}{d\xi} \psi \right) = e^{-\psi}. \quad (108)$$

Here  $x = |\mathbf{x}|$  and  $\beta = 1/T$  while  $n(0)$  and  $\Phi(0)$  are the density and the potential at the origin. Global thermodynamic magnitudes are expressed in terms of these functions evaluated at the boundary of the spherical container, thus, for convenience one introduces  $\xi_0 = (4\pi|\kappa|\beta n(0))^{1/2}R$ ,  $\psi_0 = \psi(\xi_0)$  and  $\psi'_0 = \psi'(\xi_0)$ , where primes denote the derivative with respect to  $\xi$ . Moreover, with a suitable change of variables the Emden equation can be transformed into a first order differential equation [23]. When such variables, usually denoted as  $(v, u)$ , are evaluated at  $\xi = \xi_0$  and  $\psi = \psi_0$ , with  $\psi' = \psi'_0$ , they read

$$v_0 = \xi_0 \psi'_0 \quad \text{and} \quad u_0 = \frac{\xi_0 e^{-\psi_0}}{\psi'_0}, \quad (109)$$

and therefore satisfy

$$\frac{du_0}{dv_0} = -\frac{u_0(u_0 + v_0 - 3)}{v_0(u_0 - 1)}. \quad (110)$$

On the other hand, it can be shown [4, 12] that the inverse temperature and the potential energy can be written as

$$\frac{1}{T} = \frac{R}{|\kappa|N} v_0, \quad (111)$$

$$W = NT(u_0 - 3). \quad (112)$$

What we need is to express the potential energy as a function of  $T$ ,  $P$  and  $\mu$  only. Since  $\Phi(R) = \kappa N/R$ , equations (72) and (73) yield

$$N = \frac{R}{|\kappa|} \left[ T \ln \left( \frac{P \lambda_T^3}{T} \right) - \mu \right], \quad (113)$$

where we have taken into account the local equation of state so that  $P = n(R)T$ . From (113) and (111), one sees that

$$v_0(T, P, \mu) = \ln \left( \frac{P \lambda_T^3}{T} \right) - \frac{\mu}{T}, \quad (114)$$

and therefore

$$\left( \frac{\partial v_0}{\partial T} \right)_{P, \mu} = \frac{1}{T} \left( \frac{\mu}{T} - \frac{5}{2} \right). \quad (115)$$

Combining (112) and the global equation of state (96) one obtains  $3PV = NTu_0$  and hence, taking it into account and using (111) to express  $N$ , the radius can be written as

$$R = T \left( \frac{v_0 u_0}{4\pi |\kappa| P} \right)^{1/2}. \quad (116)$$

Using (111) and (116), the potential energy (112) takes the form

$$W(T, P, \mu) = \frac{T^3 v_0^{3/2}}{(4\pi |\kappa|^3 P)^{1/2}} \left( u_0^{3/2} - 3u_0^{1/2} \right), \quad (117)$$

which depends only on the desired variables, since  $u_0 = u_0(v_0(T, P, \mu))$ . We then have

$$\left( \frac{\partial W}{\partial T} \right)_{P, \mu} = \frac{3W}{T} + \frac{3W}{2v_0} \left( \frac{\partial v_0}{\partial T} \right)_{P, \mu} \left[ 1 + \frac{v_0(u_0 - 1)}{u_0(u_0 - 3)} \frac{du_0}{dv_0} \right]. \quad (118)$$

Therefore, according to (105) and using (110), (112) and (115), from the above equation (118) the mean field entropy is obtained,

$$S = -N \left[ \frac{\mu}{T} - 2u_0 + \frac{7}{2} \right]. \quad (119)$$

Using that the thermal wavelength can be expressed as  $\lambda_T = [2\pi\hbar^2 R v_0 / (N|\kappa|m)]^{1/2}$  and that  $P/T = Nu_0/(3V)$ , from (114) one gets

$$\frac{\mu}{T} = \frac{1}{2} \ln(v_0) + \ln(v_0 u_0) - v_0 - \frac{1}{2} \ln \left( \frac{2NR^3 m^3 |\kappa|^3}{\pi \hbar^6} \right), \quad (120)$$

and thus the entropy becomes

$$S = N \left[ v_0 + 2u_0 - \frac{1}{2} \ln(v_0) - \ln(v_0 u_0) - 3 \right] + S_0, \quad (121)$$

as given in [15], with  $S_0 = N/2 \ln [2NR^3 m^3 |\kappa|^3 / (\pi \hbar^6)]$ . This verifies the first of the relations (105) for the self-gravitating gas, and the remaining two follow from an analogous procedure.

### 4.3. Small systems

Systems with a small number of constituents can be treated from a thermodynamic point of view by considering them as independent members of an ensemble. Since such an ensemble of independent small systems is a macroscopic system itself where the standard thermodynamics applies, thermodynamic properties of a single small system can be derived. This is the well known approach introduced by Hill [20]. The basic idea is to consider a ‘chemical potential’, denoted as  $\mathcal{E}$ , that accounts for the energy gained by the system when the number of members of the ensemble,  $\mathcal{N}$ , varies. The energy, volume, number of particles and entropy of each small system are  $E$ ,  $V$ ,  $N$  and  $S$ , respectively, while the total magnitudes corresponding to the whole ensemble are given by  $E_t = \mathcal{N}E$ ,  $V_t = \mathcal{N}V$ ,  $N_t = \mathcal{N}N$  and  $S_t = \mathcal{N}S$ . Since the whole ensemble is a macroscopic system, these magnitudes satisfy

$$TdS_t = dE_t + PdV_t - \mu dN_t - \mathcal{E}d\mathcal{N} \quad (122)$$

and hence,  $TS_t = E_t + PV_t - \mu N_t - \mathcal{E}\mathcal{N}$ . Thus, for any small system:

$$TS = E + PV - \mu N - \mathcal{E}, \quad (123)$$

$$TdS = dE + PdV - \mu dN, \quad (124)$$

$$d\mathcal{E} = -SdT + VdP - Nd\mu. \quad (125)$$

Hill mentioned that the use of different environmental variables, i.e. control parameters, would lead to different descriptions of the thermodynamic phenomena when small systems are considered [20]. In this case, *ensemble inequivalence* is due to the finite size of the systems. In fact, negative heat capacity leading to ensemble inequivalence is a generic feature of finite systems at phase coexistence [6]. On the other hand, systems with long-range interactions can be regarded as finite systems as well, in the sense that the range of the interaction is comparable with the size of the system [6].

Our aim here is to point out another common feature between small systems and systems with long-range interactions. Due to non-negligible self-interactions, an ensemble of independent systems with long-range interactions cannot be considered. Nonetheless, if one sets  $\mathcal{N} = 1$ , fixed, so that  $d\mathcal{N} = 0$ , and relates the energy  $\mathcal{E}$  with the potential energy such that  $\mathcal{E} = -\sigma W$ , equations (123) and (125) become the same equations as (99) and (104). Although  $W$  and  $\mathcal{E}$  are introduced for different reasons, they formally play the same role. Therefore, a small system such as a macromolecule and a system with long-range interactions such as a star, both being finite system, can be formally described by the same thermodynamic relations.

## 5. Discussion

We have studied the local thermodynamics of systems with strong long-range interactions in  $d$  dimensions by computing local thermodynamic potentials per particle in the mean field limit. We have considered pair interaction potentials that decay as  $1/r^\nu$ , with  $0 \leq \nu \leq d$ . By computing the local entropy per particle and using the condition of local thermodynamic equilibrium we have obtained the local equation of state, which corresponds to the isothermal ideal gas equation, regardless of the long-range interaction potential that couples the constituents of the system. This result coincides with the results that were obtained in previous works where the condition of hydrostatic equilibrium was assumed [14, 19]. Thus, we have shown that interactions

locally play the role of an external field that perturbs the gas and that the local entropy per particle is a function of the local kinetic energy and local volume: it is the Sackur-Tetrode entropy formulated in terms of local variables. The local entropy per particle was computed in the microcanonical ensemble and with the one-particle distribution function approach, leading to the same result.

Different ensemble representations possess, in general, different ranges of validity in the space of parameters specifying the state of the system. Since any global thermodynamic potential computed in different ensemble representations has the same functional form in the mean field limit, local thermodynamic potentials have also the same functional form in the different ensemble representations. By volume integration of the relation satisfied by the thermodynamic magnitudes at the local level, we have obtained the equation satisfied by the set of global magnitudes. Remarkably, the potential energy enters as a thermodynamic variable which modifies the global thermodynamic potentials. In the thermodynamics of systems with short-range interactions the potential energy is obviously involved since it is included in the total energy, but it does not appear as an additional contribution which modifies the thermodynamic potentials. Such a contribution is proportional to  $\sigma = (d - \nu)/\nu$  and hence, for the marginal case  $\nu = d$ , the usual thermodynamic relations valid for short-range potentials are recovered.

As a consequence of this contribution coming from the total potential energy, the Gibbs-Duhem equation is modified and the intensive variables can no longer be seen as independent if long-range interactions are present in the system. By taking advantage of the thermodynamic relations obtained from this generalized Gibbs-Duhem equation, the entropies of a system with a spatially uniform potential and of the self-gravitating gas have been computed.

## Acknowledgments

One of the authors (I L) wants to thank Markus Fröb for fruitful discussions. He also acknowledges financial support through an FPI scholarship (BES-2012-054782) from the Spanish Government. This work was supported by MICINN of the Spanish Government under grant FIS2011-22603.

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